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(54) PERFLUOROPOLYETHER-MODIFIED SILANE, SURFACE TREATING AGENT AND ANTIREFLECTION FILTER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a perfluoropolyether-modified silane which has water/oil repellency, parting properties, chemical resistance, lubricity, durability, antifouling properties and fingerprint wipe-off property due to absence of a polar group, is useful as a surface treating agent for coating the surfaces of various kinds of substrates, is applicable to an antireflection filter that has been formed with a cured coating film on the surface, is hardly stained, has the stain to be readily wiped off, is excellent in slipperiness on the surface, is hardly damaged and keeps these performances for a long period of time.

SOLUTION: The perfluoropolyether-modified silane is represented by formula (1) (Rf is a bifunctional straight-chain perfluoropolyether group; R is a 1-4C alkyl group or phenyl group; X is a hydrolyzable group; (n) is 0-2; (m) is an integer of 1-5; (a) is 2 or 3).

Rf
Rf-CO_n-O-C(=O)-Si-X_a

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CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1)

[Formula 1]



(For the alkyl group of carbon numbers 1-4 or a phenyl group, and X, a hydrolysis nature machine and n are [Rf / the straight chain mold perfluoro polyether radical of bivalence, and R / the integer of 1-5 and a of 0-2m] 2 or 3 among a formula.) The perfluoro polyether denaturation silane shown.

[Claim 2] The perfluoro polyether denaturation silane according to claim 1 characterized by the hydrolysis nature machine X being an ORGANO oxy-radical.

[Claim 3] The finishing agent which uses a perfluoro polyether denaturation silane according to claim 1 or 2 and/or its partial hydrolysis condensate as a principal component.

[Claim 4] The acid-resisting filter characterized by forming the stain-proofing barrier whose fall angle over oleic acid is 5 degrees or less and, whose rate of change of the fall angle after solvent cleaning to the fall angle before solvent cleaning is 10% or less on the surface layer of the inorganic system acid-resisting layer which has a silicon-dioxide system inorganic layer as a surface layer.

[Claim 5] The acid-resisting filter according to claim 4 characterized by the adhesive strength to the adhesive tape of a stain-proofing barrier and the adhesive strength to the adhesive tape of the stain-proofing barrier after solvent cleaning being 0.2Ns / 19mm or less, respectively.

[Claim 6] The acid-resisting filter according to claim 4 or 5 with which a stain-proofing barrier is characterized by being formed using a perfluoro polyether denaturation silane and/or its partial hydrolysis condensate.

[Claim 7] A perfluoro polyether denaturation silane is the following general formula (1).

[Formula 2]



(-- for the alkyl group of carbon numbers 1-4 or a phenyl group, and X, a hydrolysis nature machine and n are [Rf / the straight chain mold perfluoro polyether radical of bivalence, and R / the integer of 1-5 and a of 0-2m] 2 or 3 among a formula.) -- acid-resisting filter according to claim 6 characterized by being the compound shown.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the acid-resisting filter which has the stain-proofing barrier which was excellent in the finishing agent and list which make a principal component the new perfluoro polyether denaturation silane and this new which were excellent in water and oil repellency, a mold-release characteristic, chemical resistance, lubricity, etc., and excellent in endurance, antifouling property, especially fingerprint wiping nature at antifouling property and fingerprint wiping nature, and was excellent in especially endurance.

[0002]

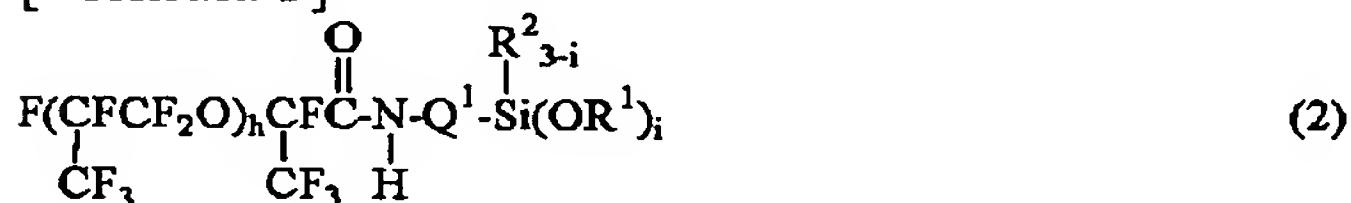
[Description of the Prior Art] Generally, since the surface energy of a perfluoro polyether radical content compound is very small, it has water and oil repellency, chemical resistance, lubricity, a mold-release characteristic, antifouling property, etc. It is industrially used for water-and-oil-repelling stain proofing agents, such as paper and fiber, the lubricant of a magnetic-recording medium, the oil-repellent agent of a precision mechanical equipment, a release agent, cosmetics, a protective coat, etc. broadly using the property.

[0003] However, even if it is shown that the property has the non-adhesiveness over other base materials and non-adhesion in coincidence and it could apply to the base material front face, it was difficult to form and stick a coat.

[0004] On the other hand, as what combines a base material front face and organic compounds, such as glass and cloth, the silane coupling agent is known well. A silane coupling agent has an organic functional group and a reactant silyl radical (generally alkoxy silyl radical) in 1 molecule. With the moisture in air etc., an alkoxy silyl radical causes a self-condensation reaction, serves as a siloxane, and forms a coat. it becomes the firm coat which has endurance by combining with front faces, such as it, simultaneously a glass metallurgy group, chemically and physically. The silane coupling agent is broadly used as a coating agent on the various front faces of a base material using this property.

[0005] As what employed these descriptions efficiently, it is the following formula (2) at JP,58-167597,A.

[Formula 3]



(-- the inside of a formula, and R1 and R2 -- the alkyl group of carbon numbers 1-4, and Q1 -- CH₂CH₂CH₂ or CH₂CH₂NHCH₂CH₂ -- the integer of 1-4 and i of CH₂ and h are 2 or 3.) -- the fluoro amino silane compound shown is indicated. However, since this compound had the part of a perfluoro polyether radical as short as 2 of hexafluoropropylene oxide (HFPO) - a pentamer, it was not fully able to take out the description which the above-mentioned perfluoro polyether radical has.

[0006] Moreover, at JP,58-122979,A, it is the following type (3) as a water and oil repellent agent on the front face of glass.

[Formula 4]



(Among a formula, Rf1 is the poly fluoro alkyl group of 1-20 carbon numbers, and may also include one or more ether linkage.) R3 an alkylene group and X1 for a hydrogen atom or a low-grade alkyl group, and A -

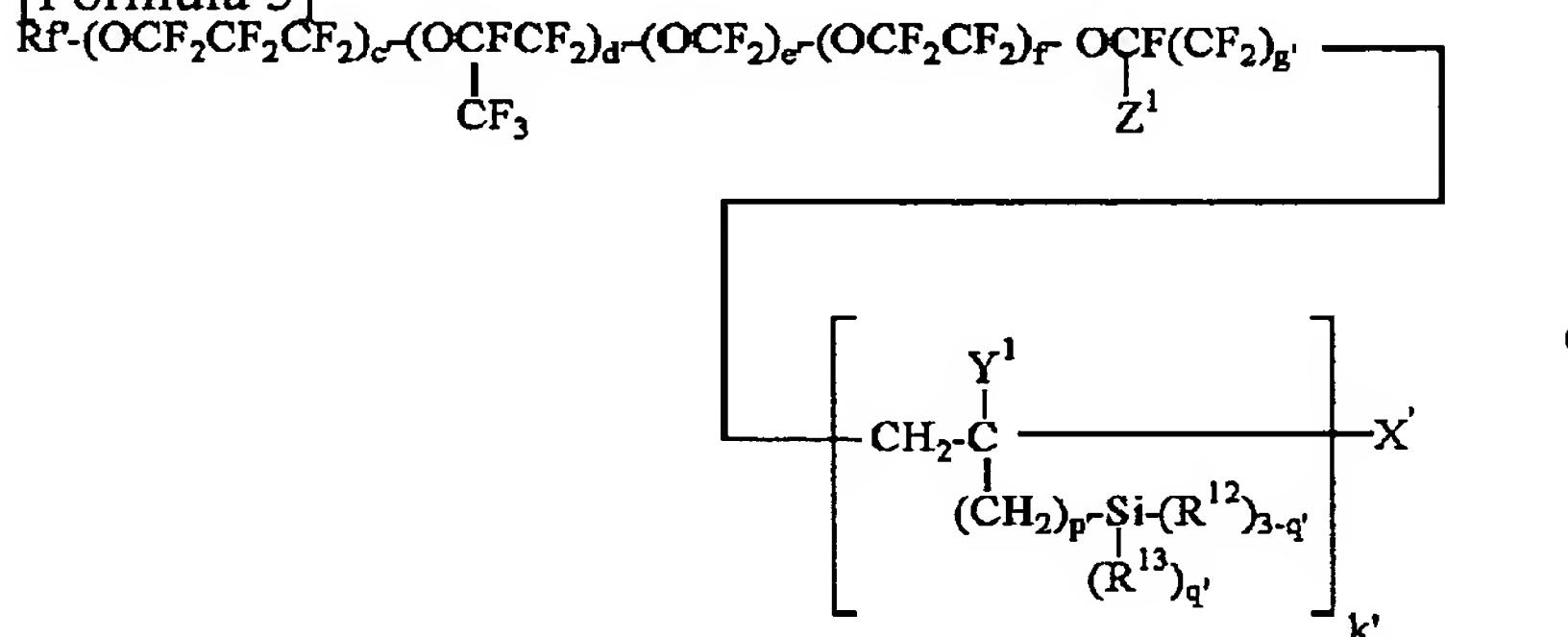
CON(R4)-Q- or SO₂N(R4)-Q- (however, R4 shows a low-grade alkyl group, and Q shows a divalent organic radical) and Z -- a low-grade alkyl group and Y -- a halogen, an alkoxy group, or R5 -- the integer of COO, - (however, R5 shows a hydrogen atom or a low-grade alkyl group), s0, or 1 and t show the integer of 1-3, and u shows the integer of 0, or 1-2. Although the compound shown is shown, in this case, there are few carbon numbers of the part of a fluorine-containing radical as 1-20 pieces, and sufficient effectiveness is not acquired, either.

[0007] Recently, in order to improve maintenance-free-izing a windowpane especially with upper-layers-izing of a building, an appearance, and visibility, the demand to the technique "it is dirt-hard and carries out" which a fingerprint makes it hard to be attached on the surface of a display, and the technique "which dirt is made easy to remove" was increasing every year, and development of the ingredient which can meet these demands was desired.

[0008] Taking advantage of the property of the above-mentioned perfluoro polyether radical content compound and a silane coupling agent, a firm coat is formed in a base material front face, and the lens which used for the stain-proofing barrier the fluorine-containing shiran compound expressed with the following type (4) as a finishing agent excellent in water and oil repellency, antifouling property, chemical resistance, lubricity, a mold-release characteristic, etc. is known (JP,9-258003,A).

〔0009〕

[Formula 5]



inside of formula, and Rf -- the shape of a straight chain of carbon numbers 1-16, and the letter perfluoroalkyl radical of branching -- X' hydrogen or a low-grade alkyl group, and Z1 for iodine or hydrogen, and Y1 A fluorine or a trifluoromethyl radical, as for 0 or 1, p', and q', the radical which can hydrolyze R12, and R13 show [hydrogen or the inactive organic radical of monovalence c', d', and f'] the integer of 1-10 for the integer of 0-200, and g', as for the integer of 0-2, and k'.

[0010] however, although there be comparatively many fluorine-containing shiran compounds express with the above-mentioned general formula (4), when especially the adhesion to a base material be inadequate, there be a problem in respect of endurance and it used as a finishing agent of a lens from exist only in a piece end, the content rate of the hydrolysis nature machine in 1 molecule may make a desired engine performance maintain over a long period of time, and they be able to say it with a suitable thing -- .

[0011] Moreover, if it is in a common antireflection film to be prepared in front faces, such as check-by-looking equipment Contaminations, such as finger marks, a fingerprint and sweat, and saliva, a charge for a haircut, tend to adhere. A surface reflection factor changes by the adhesion, or Offer of the antireflection film which is excellent in the adhesion tightness of this contamination or the removal nature of adhesion contamination since there is a difficulty that contamination tends to be conspicuous compared with the case of a mere transparency plate -- an affix looms white, it is visible and the contents of a display become indistinct -- etc. has been a long technical problem.

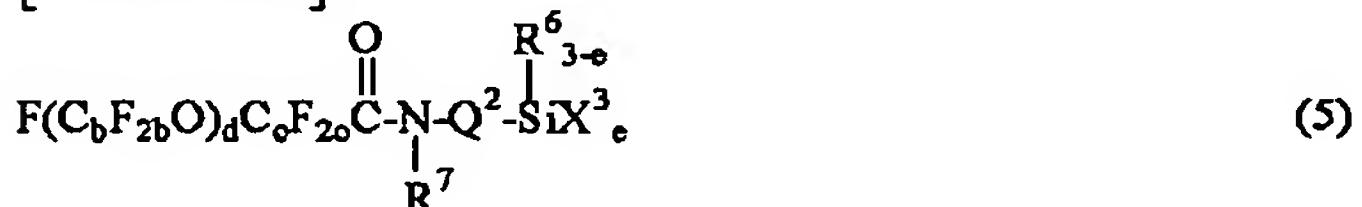
[0012] What has the hardening layer which becomes the front face of the acid-resisting layer which consists of the monolayer or the multilayer inorganic layer which has the surface layer which uses as a principal component conventionally the silicon dioxide formed by PVD as an antireflection film aiming at contamination-resistant improvement etc. from an organic polysiloxane system polymerization object or a perfluoroalkyl radical content polymerization object was known (JP,6-5324,B).

[0013] However, since an antireflection film would get damaged if it is difficult to wipe off with tissue paper etc., contamination can extend to a thin film and it grinds strongly when body-contamination of finger marks, a fingerprint, etc. adheres, there was a trouble that satisfying removal could not be attained.

[0014] Generally, a perfluoro polyether radical content compound has the above-mentioned description, and the antireflection film which used for the stain-proofing barrier the perfluoro polyether denaturation amino

silane shown by the following formula (5) is indicated by JP,11-29585,A as what employed these descriptions efficiently. This antireflection film However, water and oil repellency, antifouling property, chemical resistance, lubricity, Although excelled in the mold-release characteristic etc., polar groups, such as an amide group with high compatibility with water, are contained in the molecule of the perfluoro polyether denaturation amino silane used for the stain-proofing barrier. Moreover, since [of the hydrolysis nature machine in 1 molecule] it is comparatively (% of the weight) few, To give still more sufficient engine performance, when it has troubles, such as requiring time amount and a point of the adhesion to a base material, and uses as a finishing agent by hardening was desired.

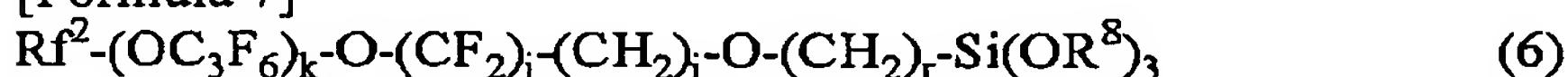
[Formula 6]



(X3 a hydrolysis nature machine and R6 a low-grade alkyl group and R7 a hydrogen atom or a low-grade alkyl group, and Q2 inside of a formula, CH₂ CH₂ CH₂ or CH₂CH₂NHCH₂ CH₂ CH₂ and d the integer of 6-50 and e 2 or 3, and b and c respectively integer of 1-3.)

[0015] moreover, in JP,2001-188102,A The acid-resisting film which used for the stain-proofing barrier the perfluoro polyether radical content silane coupling agent shown by the following formula (6) is indicated. The perfluoro polyether radical content silane coupling agent used for this stain-proofing barrier Although the polar group was not contained, it could not say that the rate of the hydrolysis nature machine in 1 molecule was enough, and it was not able to be referred to as having sufficient engine performance, when using as a finishing agent that requiring time amount by hardening and the adhesion to a base material were inferior etc.

[Formula 7]



(However, Rf2 is 0<j+i<=6 although the integer of 1-50 and r are [the shape of a straight chain of carbon numbers 1-16, the letter perfluoroalkyl radical of branching, and R / the integer of 0-3 and i of the integer of 0-6 and j] the integers of 0-3 for the alkyl group of carbon numbers 1-10, and k.)

[0016] Therefore, also when contamination cannot adhere easily and contamination adheres, while the contamination cannot be easily conspicuous The contamination which adhered also including body-contamination of finger marks, a fingerprint, etc. is wiped off easily, and tissue paper etc. can remove it. It was hard to get damaged by the wiping actuation, and adhesion of waterdrop etc. could be easily shaken off and development of the acid-resisting filter which moreover maintains engine performance, such as this resistance to contamination, ***** removal nature, abrasion-proof nature, and water repellence, at a long period of time was desired.

[0017]

[Patent reference 1] JP,58-167597,A [the patent reference 2] JP,58-122979,A [the patent reference 3] JP,9-258003,A [the patent reference 4] JP,6-5324,B [the patent reference 5] JP,11-29585,A [the patent reference 6] JP,2001-188102,A [0018]

[Problem(s) to be Solved by the Invention] Therefore, this invention aims at offering the acid-resisting filter which has the stain-proofing barrier which was excellent in the finishing agent and list which make a principal component the new perfluoro polyether denaturation silane and this new which were excellent in water and oil repellency, a mold-release characteristic, chemical resistance, lubricity, etc. in order to meet the above-mentioned request, and were excellent in endurance, antifouling property, especially fingerprint wiping nature at antifouling property and fingerprint wiping nature, and was excellent in especially endurance on a front face.

[0019]

[The means for solving a technical problem and the gestalt of implementation of invention] this invention person is the following general formula (1), as a result of inquiring wholeheartedly, in order to meet the above-mentioned request.

[Formula 8]



the inside of a formula, and Rf -- the straight chain mold perfluoro polyether radical of bivalence, and R --

the alkyl group of carbon numbers 1-4, or a phenyl group -- for X, a hydrolysis nature machine and n are [the integer of 1-5 and a of 0-2m] 2 or 3. The new perfluoro polyether denaturation silane expressed Water and oil repellency, It excels in a mold-release characteristic, chemical resistance, lubricity, endurance, antifouling property, especially fingerprint wiping nature, and can use as a finishing agent, the knowledge of being suitable for forming the hardening film in the front face of an acid-resisting filter is carried out, and it came to make this invention.

[0020] Moreover, the thing for which a stain-proofing barrier is formed on the surface layer of the inorganic system acid-resisting layer which has a silicon-dioxide system inorganic layer, A stain-proofing barrier using the silane of the above-mentioned formula (1) by in this case, the thing which the fall angle over oleic acid is 5 degrees or less, and the rate of change of the fall angle after solvent cleaning to the fall angle before solvent cleaning considers as 10% or less of thing Surface energy is small and the effectiveness continues to the top where the adhesion force of a pollutant is small. Adhesion of pollutants, such as a fingerprint, sebum, sweat, and cosmetics, is prevented. Moreover, again Even if it adheres, it can wipe off easily, and there are few depressions of the stain-proofing barrier by scratch, a blemish cannot be easily attached to an acid-resisting layer front face, the knowledge of the acid-resisting filter which can prevent exfoliation of the acid-resisting layer taking advantage of a blemish being obtained is carried out, and it came to make this invention.

[0021] Therefore, this invention offers the perfluoro polyether denaturation silane of the above-mentioned general formula (1). Moreover, the finishing agent which uses this perfluoro polyether denaturation silane and/or its partial hydrolysis condensate as a principal component, On the surface layer of the inorganic system acid-resisting layer which has a silicon-dioxide system inorganic layer as a surface layer in a list The stain-proofing barrier whose fall angle over oleic acid is 5 degrees or less and whose rate of change of the fall angle after solvent cleaning to the fall angle before solvent cleaning is 10% or less, The acid-resisting filter characterized by forming the stain-proofing barrier using the silane and/or its partial hydrolysis condensate of the above-mentioned formula (1) especially is offered.

[0022] Hereafter, lessons is taken from this invention and it explains in more detail. The perfluoro polyether denaturation silane of this invention is shown by the following general formula (1).

[0023]

[Formula 9]



(For the alkyl group of carbon numbers 1-4 or a phenyl group, and X, a hydrolysis nature machine and n are [Rf / the straight chain mold perfluoro polyether radical of bivalence, and R / the integer of 1-5 and a of 0-2m] 2 or 3 among a formula.)

[0024] Here, Rf is the straight chain mold perfluoro polyether radical of bivalence, and although various chain length's perfluoro polyether radical is contained, it is the straight chain mold perfluoro polyether of the bivalence which makes a repeating unit preferably a with a carbon number of about one to four perfluoro polyether radical. As a straight chain mold perfluoro polyether of this bivalence, a thing as shown below is mentioned, for example.

- CF₂CF₂O(CF₂CF₂CF₂O) _kCF₂CF₂ -- k, p, and q in the CF₂(OC₂F₄) _p-(OCF₂) _q-above-mentioned chemical structure type show one or more integers, respectively. concrete -- 1-50 -- the range of 10-40 is more preferably desirable. In addition, the molecular structure of a perfluoro polyether is not limited to what was these-illustrated.

[0025] X expresses a hydrolysis nature machine. As the example, halogen radicals, such as alkenyloxy radicals, such as acyloxy radicals, such as alkoxy alkoxy groups, such as alkoxy groups, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, a methoxy methoxy group, and a methoxyethoxy radical, and an acetoxy radical, and an isopropanal PENOKISHI radical, the Krol radical, a BUROMO radical, and an iodine radical, etc. are mentioned. Especially, ORGANO oxy-radicals, such as an alkoxy group and an alkenyloxy radical, and the Krol radical are desirable, and a methoxy group, an ethoxy radical, an isopropanal PENOKISHI radical, and the Krol radical are especially desirable.

[0026] It is the low-grade alkyl group or phenyl group of carbon numbers 1-4, and R is specifically a methyl group, an ethyl group, a phenyl group, etc., and a methyl group is suitable for it especially. n is the integer of 0-2 and 1 is desirable. Moreover, m is the integer of 1-5 and 3 is desirable. a is 2 or 3 and the viewpoint of reactivity and the adhesion over a base material to 3 is desirable.

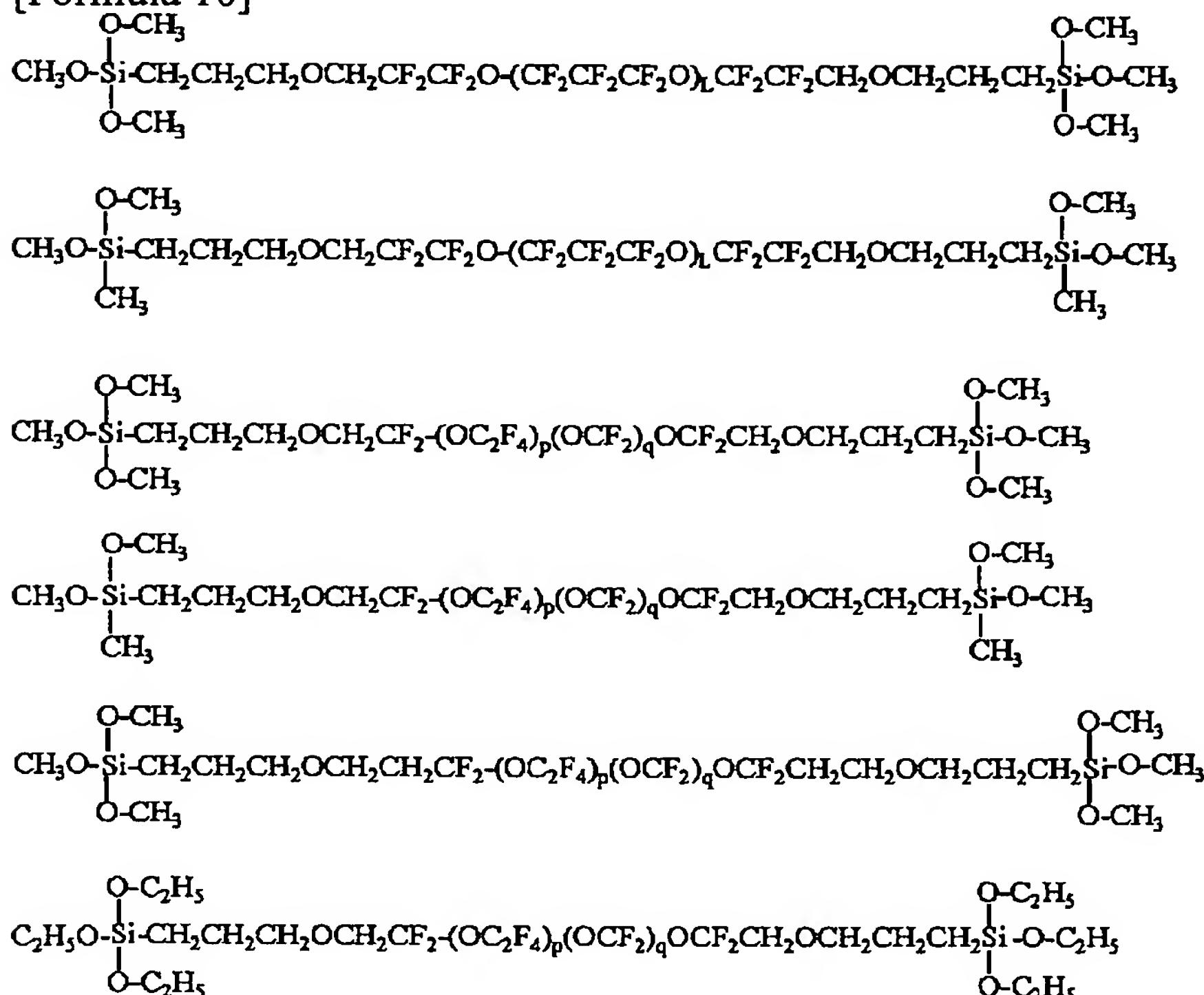
[0027] although especially the molecular weight of the perfluoro polyether denaturation silane compound of

this invention is not restricted -- the point of stability, the ease of dealing with it, etc. to number average molecular weight -- 500-20,000 -- the thing of 1000-10,000 is preferably suitable.

[0028] As an example of the above-mentioned perfluoro polyether denaturation silane, what is shown with the following structure expression is mentioned, for example. However, it is not limited to the following instantiation.

[0029]

[Formula 10]

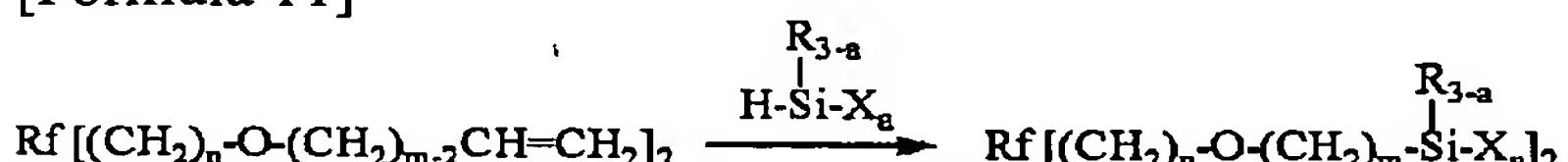


(For L, 1-50p is [the sum of 1-50, and p+q of 1-50q] the integers of 10-100 among the above-mentioned formula, and the array of the repeat unit in a formula is random.) Even when these are independent one sort, even if they combine two or more sorts, they can be used.

[0030] As the manufacture approach of the perfluoro polyether denaturation silane of this invention, the approach to which the hydrosilane which has a hydrolysis nature machine is made to add from the conventional method of hydrosilylation using a platinum system catalyst is in the perfluoro polyether which contains alpha-unsaturated bond in both ends, for example.

[0031]

[Formula 11]



(Rf, R, X, n, m, and a are the same as the above among a formula.)

[0032] Here as the synthetic approach of the perfluoro polyether which contains alpha-unsaturated bond in the above-mentioned both ends The both-ends alcoholic denaturation perfluoro polyether expressed with the following formula (7) It is made to react with alkali-metal hydroxides, such as alkali metal, such as K, Na, and Li, KOH, NaOH, and LiOH. The both-ends alcholate denaturation perfluoro polyether expressed with a formula (8) is made to generate, and it is obtained by next making this both-ends alcholate denaturation perfluoro polyether react with alpha-unsaturated bond content halogenide.

Rf[(CH₂)_n-OH] 2 (7) Rf[(CH₂)_n-OM] 2 (8) (the inside of a formula, and n -- the above -- the same -- M is alkali metal.)

[0033] Since the polar group which can serve as an adverse element in respect of a property is not included at all in a molecule, the perfluoro polyether denaturation silane of this invention is excellent in water and oil repellency, antifouling property, chemical resistance, lubricity, a mold-release characteristic, etc., and can be used as a finishing agent by coating various base material front faces. Moreover, it has at least two hydrolysis nature machines, such as a silyl radical of hydrolysis nature, at a time in the both ends of a

molecule, and since both ends have stuck to the base material firmly, the effectiveness can be made to maintain for a long period of time.

[0034] The following is mentioned as an application using this function.

Water and oil repellent agent -- Release agents, such as paper, cloth, a metal, and a glass plastics ceramic -- Soil-resistant-finish agents, such as - resin molding die, an object for a roll, etc. for adhesive tape -- It is lubricative improvement in reforming, a tape film, etc. about the fluidity and the dispersibility of -- coating additives, such as paper, cloth, a metal, and a glass plastics ceramic, a resin modifier, and a minerals filler.

[0035] The perfluoro polyether denaturation silane of this invention is suitably used as a finishing agent, and can form a hardening coat in the front face of an acid-resisting filter. The finishing agent of this invention uses as a principal component the perfluoro polyether denaturation silane shown in the formula (1) of this invention, and/or its partial hydrolysis condensate.

[0036] In this finishing agent, an ORGANO oxy-silane hydrolysis condensation catalyst may be added if needed. As an ORGANO oxy-silane hydrolysis condensation catalyst, inorganic acids, such as organic acids, such as organic titanium compounds, such as organic tin compounds, such as dibutyl tin dimethoxide and JIRAUIN acid dibutyl tin, and tetra-n-butyl titanate, an acetic acid, and methansulfonic acid, a hydrochloric acid, and a sulfuric acid, are mentioned. An acetic acid, tetra-n-butyl titanate, JIRAUIN acid dibutyl tin, etc. are especially desirable. It is the usual amount of catalysts, 0.01 - 5 weight section of an addition is desirable to a perfluoro polyether denaturation silane and/or its partial hydrolysis condensate 100 weight section, and its 0.1 - 1 weight section is especially desirable.

[0037] Moreover, although the processing agent of this invention may use a perfluoro polyether denaturation silane and/or its partial hydrolysis condensate as it is, it may dilute with a suitable solvent and it may be used with it. Two or more sorts of partially aromatic solvents are sufficient as a solvent, and what dissolves a perfluoro polyether denaturation silane and/or its partial hydrolysis condensate in homogeneity is desirable.

[0038] As a solvent, fluorine denaturation aliphatic hydrocarbons, such as a perfluoro heptane and a perfluoro octane, a meta xylene hexa flora -- fluorine denaturation aromatic hydrocarbons solvents, such as id and benzotrifluoride, -- Fluorine denaturation ethers solvents, such as methyl perfluoro butyl ether and perfluoro (2-butyl tetrahydrofuran), Fluorine denaturation alkylamine system solvents, such as perfluoro tributylamine and perfluoro tripentylamine, Ketones, such as hydrocarbon system solvents, such as petroleum benzine, mineral spirits, toluene, and a xylene, an acetone, a methyl ethyl ketone, and methyl isobutyl ketone, are mentioned. the solvent by which fluorine denaturation was carried out in respect of solubility, wettability, etc. -- desirable -- especially -- a meta xylene hexa flora -- the id, perfluoro (2-butyl tetrahydrofuran), and perfluoro tributylamine are desirable.

[0039] As an approach of forming a coat, it can process by well-known approaches, such as brush coating, dipping, a spray, and vacuum evaporationo processing. Although the optimal temperature changes with arts in processing temperature, in the case of brush coating or dipping, the range of 120 degrees C is desirable from a room temperature, for example. Although processing humidity is desirable when carrying out under humidification promotes a reaction, it is desirable to optimize each time with the silane compound to be used or other additives.

[0040] As a base material which forms a coat, the thing of the various quality of the materials, such as paper, cloth, a metal and its oxide, glass, plastics, pottery, and a ceramic, can be used.

[0041] Here as goods which form a hardening coat in a front face Optical members, such as a glasses lens and an acid-resisting filter (a fingerprint, sebum antisticking coating), An organ bath, a sanitary product like a washstand (water-repellent ** antifouling coating), Windowpanes, such as an automobile, an electric car, and an aircraft, head-lamp covering (antifouling coating), etc., The building materials for outer walls (water-repellent ** antifouling coating), the building materials for kitchens (coating for oil dirt prevention), A telephone booth (water-repellent ** antifouling and poster prevention coating), a work of art, etc. have a compact disk (hydrofuge, oil repellency, and coating of fingerprint antisticking grant), desirable DVD (fingerprint antisticking coating), etc. The finishing agent of this invention is suitable to form a coat in optical members, such as a lens and a filter, and give acid resistibility, antifouling property, etc. especially.

[0042] This invention offers the acid-resisting filter which has the hardening coat of the perfluoro polyether denaturation silane of an acid-resisting filter, especially the above-mentioned formula (1), and/or its partial hydrolysis condensate on a front face further. In this case, the acid-resisting filter of this invention is characterized by using the thing whose fall angle over oleic acid are the thing in which the stain-proofing barrier was formed on the front face of the acid-resisting layer which has a silicon-dioxide system inorganic layer as a surface layer, and is 5 degrees or less as said stain-proofing barrier and whose rate of change of

the fall angle after solvent cleaning to the fall angle before solvent cleaning is 10% or less.

[0043] Here, 5 degrees or less of fall angles [as opposed to oleic acid in a stain-proofing barrier] are 3 degrees or less preferably, and the rate of change of the fall angle after solvent cleaning to the fall angle before solvent cleaning is 5% or less preferably 10% or less. If the fall angle over oleic acid is larger than 5 degrees, it may be lacking in contamination tightness, and a fingerprint etc. may especially tend to adhere, and it may become scarce at the wiping nature of contamination, and may be lacking in the slipping nature in the front face in the case of wiping.

[0044] If [(B-A) /rate-of-change A] x100 of the fall angle B after solvent cleaning to the fall angle A before solvent cleaning exceed 10%, it may be lacking in endurance about contamination tightness and fingerprint wiping nature. In addition, the fall angle over oleic acid is measured with the contact angle plan usually used. Moreover, solvent cleaning is lightly performed by the ***** approach after immersion for 5 minutes into an applicable solvent, a solvent is used by the usual washing, and HCFC-225, nona fluoro butyl methyl ether, etc. are easy to be mentioned.

[0045] Moreover, it is desirable that the adhesive strength to the adhesive tape of a stain-proofing barrier and the adhesive strength to the adhesive tape of the stain-proofing barrier after solvent cleaning are 0.2Ns / 19mm or less, respectively. If the adhesive strength to the adhesive tape of a stain-proofing barrier is larger than 0.2Ns / 19mm, it may be lacking in fingerprint wiping nature. On a stain-proofing barrier front face, the adhesive strength to the adhesive tape of a stain-proofing barrier is polyester adhesive tape, and is measured by exfoliation rate 300 mm/min at the include angle of 180 degrees using a tension tester.

[0046] In this case, as for a stain-proofing barrier, being formed using a perfluoro polyether denaturation silane is desirable, and the perfluoro polyether denaturation silane shown by the same following general formula (1) especially as the above-mentioned or its hardening coat of that partial hydrolysate is desirable.

[Formula 12]



(For the alkyl group of carbon numbers 1-4 or a phenyl group, and X, a hydrolysis nature machine and n are [Rf / the straight chain mold perfluoro polyether radical of bivalence, and R / the integer of 1-5 and a of 0-2m] 2 or 3 among a formula.)

[0047] As an approach of forming a stain-proofing barrier, processings of a well-known approach, such as brush coating, dipping, a spray, and vacuum evaporationo processing, are mentioned. In processing temperature, the optimal temperature changes with arts, for example, in the case of brush coating or dipping, the range of 120 degrees C is desirable from a room temperature. Although processing humidity is desirable when carrying out under humidification promotes a reaction, it is desirable to optimize each time with the silane compound and other additives to be used, since processing conditions differ.

[0048] In such spreading, although a perfluoro polyether denaturation silane may be used as it is, you may dilute and use with a suitable solvent. Two or more sorts of mixed solvents are sufficient as a solvent, and what dissolves a perfluoro polyether denaturation silane in homogeneity is desirable.

[0049] The thing same as a solvent as the above-mentioned solvent can be used. Furthermore, the same ORGANO oxy-silane hydrolysis condensation catalyst as the above-mentioned thing may be added if needed.

[0050] In addition, although the thickness of a stain-proofing barrier is selected suitably, 1-100nm is usually especially desirable [thickness] 0.1nm - 5 micrometers.

[0051] Although the acid-resisting filter of this invention is an acid-resisting filter which forms a stain-proofing barrier as mentioned above on the surface layer of the inorganic system acid-resisting layer which has a silicon-dioxide system inorganic layer as a surface layer, as for an inorganic system acid-resisting layer, it is desirable to prepare through interlayers, such as a direct or rebound ace court layer, in this case on a support base material. Drawing 1 and 2 show this and, for one in drawing, as for an interlayer and 3, a support base material and 2 are [an inorganic system acid-resisting layer and 4] stain-proofing barriers.

[0052] An inorganic system acid-resisting layer is a part which bears a substantial acid-resisting function here, and in this invention, although it can consider as the proper structure of monolayer structure or double layer structure, the surface layer of an antireflection film is a silicon-dioxide system inorganic layer.

[0053] Therefore, as an inorganic system acid-resisting layer, it can form as an acid-resisting layer of the structure according to the former, for example like the conventional technique based on JP,58-46301,A, JP,59-49501,A and JP,58-50401,A, JP,1-294709,A, JP,6-5324,B, etc.

[0054] As for an acid-resisting layer, considering as double layer structure is desirable, and it is more

desirable than points, such as the acid-resisting effectiveness, to consider as the double layer structure in which the layer of a refractive index higher than the silicon-dioxide system inorganic layer of a surface layer was made especially inherent one layer or more than two-layer. In that case, about the thickness of each class, or a setup of a refractive index, it can apply to a well-known technique correspondingly.

[0055] The inorganic substance which consists of an inorganic oxide, inorganic halogenides, those composites, etc. can be used for formation of an inorganic system acid-resisting layer. As the example, the inorganic halogenide of the inorganic oxide of SiO_2 , ZrO_2 , aluminum O_3 , Y_2O_3 , and TiO_2 grade, MgF_2 , BaF_2 , CaF_2 , LaF_2 , LiF and NaF , and SrF_2 grade etc. is mentioned as an example of representation.

[0056] Although the inorganic substance which forms an acid-resisting layer is used in the proper condition, such as dispersion liquid which its one sort or two sorts or more mixed with the polymer for a solid-state object or binders etc. according to the following formation approach etc., it is more desirable than points, such as a degree of hardness and resistance to contamination, to use an inorganic substance by the presentation contained 30% of the weight or more in that case. In addition, although a proper polymer can be used as a polymer for binders and there is especially no limitation, the organic silicon compound of the various kinds which can form polyorganosiloxane, its hydrolyzate, etc. are more desirable than points, such as a degree of hardness.

[0057] various kinds of PVD(s) (Physical Vapor Deposition) by which formation of an inorganic system acid-resisting layer is represented with vacuum evaporation technique, the sputtering method, the ion plating method, etc. -- it can carry out by the thin film forming method with the proper fluid applying method represented with law or a spin coat method, the immersion coat method, the curtain flow coat method, the roll coat method, a spray coating method, a flow-coating method, etc.

[0058] As for the silicon-dioxide system inorganic layer from which an inorganic oxide of SiO_2 grade, an inorganic halogenide of MgF_2 grade, etc. which were illustrated above are preferably used by PVD, and serve as especially a surface layer at it, what was formed in the layer which contains a silicon dioxide as a principal component by PVD is more desirable than points, such as height of surface hardness, and the adhesion of a stain-proofing barrier.

[0059] Moreover, in order to prevent adhesion of the dust by electrification etc., the conductive layer which also demonstrates the removal effectiveness of static electricity and the shielding effect of an electromagnetic wave may be included in an inorganic system acid-resisting layer. This conductive layer is formed as transparency electric conduction film which consists of inorganic oxide thin films, such as metal thin films, such as gold, silver, and aluminum, tin oxide, indium oxide, and those mixture (ITO), etc. Especially the transparency electric conduction film of an inorganic oxide system with very little absorption of light is desirable in a visible region.

[0060] Although a thing proper as a support base material may be used on the other hand and there is especially no limitation, when forming the antireflection film with a liquefied coating method etc., the support base material which consists of glass or plastics is used preferably. In addition, although the acid-resisting filter which comes to prepare the inorganic system acid-resisting layer 3 in one side of the support base material 1 was illustrated by a diagram, the inorganic system acid-resisting layer 3 may be formed in one side or both sides of the support base material 1.

[0061] When a support base material is a glass base material, it is more desirable than the point of acquiring a high reflection effect etc. to include what shows the low refractive index of MgF_2 or CaF_2 grade in an acid-resisting layer. Moreover, in the case of a plastics base material, it is more desirable than points, such as endurance, to include what has a degree of hardness comparatively low a refractive index like SiO_2 and high in an acid-resisting layer. As an example of plastics, acetate system resin, such as polyester system resin, such as acrylic resin, diethylene-glycol bisallyl carbonate resin, polycarbonate system resin, polyethylene terephthalate, and unsaturated polyester, and triacetyl cellulose, styrene resin, polyvinyl chloride system resin, etc. are mentioned, for example.

[0062] A support base material may have proper gestalten, such as a film, a sheet, and a plate, and the thickness is arbitrary. Moreover, a support base material may have a rebound ace court layer as an interlayer. In this case, it becomes the acid-resisting layer 3 and the acid-resisting filter of the gestalt which has the rebound ace court layer 2 between the support base materials 1 like the instantiation to drawing 2.

[0063] A rebound ace court layer can also be formed according to the former. For example, the rebound ace court layer which consists of an organic silicon compound especially an organic silicon compound shown by the following general formula (9), or a hardened material of the partial hydrolysis condensate is desirable. $\text{R}_9\text{fR}_{10}\text{gSi}(\text{OR}_{11})_4\text{-f-g}$ (R_9 and R_{10} are hydrocarbon groups which have an alkyl group, an alkenyl radical, an aryl group or a halogen radical, an epoxy group, a glycidoxyl radical, the amino group, a sulphydryl

group, a metacryloxy radical, a cyano group, etc. among a formula, and R11 is the alkyl group of carbon numbers 1-8, an alkoxyalkyl group, an acyl group, or an aryl group.) (9) g is f,0, or 1 and f+g is 0, 1, or 2. [0064] Rebound ace court layers are the method of making particles, such as silica metallurgy group oxide whose mean particle diameter is 0.5-5 micrometers, contain with a sol-gel method etc. or a buff, corona discharge, and a proper approach like ion etching, and the method used as the concavo-convex front face whose center line average of roughness height is 0.01-0.5 micrometers can also attach them as what has an anti-dazzle function.

[0065] Furthermore, as an interlayer, the support base material was replaced with the rebound ace court layer, or for the purpose of the improvement in the adhesion of an antireflection film, a degree of hardness and chemical resistance, endurance, a dye affinity, etc., it could have the proper coat layer and surface treatment of it could be carried out with the rebound ace court layer.

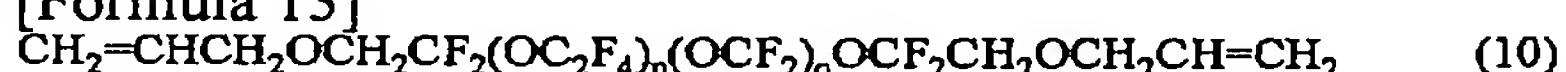
[0066] In addition, the proper ingredient for the raise in a degree of hardness indicated by JP,50-28092,B, JP,50-28446,B, JP,50-39449,B, JP,51-24368,B, JP,57-2735,B, JP,52-112698,A, etc. can be used for improvement in a degree of hardness. Moreover, the attachment of acrylic bridge formation objects, such as a bridge formation object by the approach of coating the oxide of metals, such as titanium, aluminum, and tin, or silicon, the pentaerythritol of an acrylic acid (meta), etc., etc. is effective in improvement in a degree of hardness.

[0067]

[Example] Although a synthetic example, an example, and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, in the following example, the section shows the weight section.

[0068] Perfluoro polyether 160g which has alpha-unsaturated bond in the both ends expressed with the [synthetic example] following type (10), Trimethoxysilane 15g is dropped at 0.1g of catalysts which denaturalized meta-xylene hexa FURORAIDO 80g and chloroplatinic acid by $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)2\text{OSi}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$ under 70-degree-C desiccation Ayr ambient atmosphere. After carrying out a churning reaction for 8 hours, when the solvent was distilled off, 165g (viscosity: 45.5cSt, specific gravity: 1.730, refractive-index: 1.305) of transparent and colorless liquids shown by the following formula (11) was obtained.

[Formula 13]



(11)

$$p/q \approx 0.9 \quad p+q \approx 4.5$$

[0069] On the [example 1] PET film (thickness: 100 micrometers) base material, the hydrolyzate of the silica sol 135 weight section and the gamma-glycidoxyl propyltriethoxysilane 129 weight section and the hydrolyzate of the gamma-chloropropyltrimetoxysilane 70 weight section were applied and hardened in the ethanol solution which mainly becomes, and the rebound ace court layer with a thickness of 3 micrometers was formed. The laminating of the five layers, SiO two-layer, TiO two-layer, SiO two-layer, TiO two-layer, and SiO two-layer, was carried out one by one by lambda / 4 optical thickness by the sputtering method on it, respectively, and the acid-resisting layer was attached. Next, perfluoro ether denaturation silane 0.2g of the compound 1 expressed with the above-mentioned formula (11) obtained in the synthetic example was dissolved in perfluoro (2-butyl tetrahydrofuran) 99.8g, and the coating solution was prepared. Carried out coating of this processing liquid to the aforementioned acid-resisting layer with the spin coat method, and leave it for 24 hours, it was made to harden under 25 degrees C and the ambient atmosphere of 70% of humidity, and the stain-proofing barrier was made to form. Following the (1) - (3) was evaluated using this test piece. A result is shown in Table 1.

[0070] (1) The fall angle over the stain-proofing barrier of an oleic acid drop which consists of magnitude with a diameter of 2mm was measured using the evaluation ** fall angle contact angle meter (CA-A mold by the consonance interface science company) of a surface characteristic. It measured in five places from which it differs on a front face, and the average showed.

** Polyester adhesive tape (No[by NITTO DENKO CORP.] .31B, width of face of 19mm) was stuck on the adhesive strength stain-proofing barrier front face, and the adhesive strength was measured. Exfoliation

rate 300 mm/min performed measurement at the include angle of 180 degrees using the tension tester.
 (2) After carrying out after [immersion] drawing desiccation of the evaluation test piece of the endurance of a coat for 5 minutes at a fluorine system solvent (AK[by the Asahi glass company]- 225), a fall angle and adhesive strength were measured by the approach shown by above-mentioned measurement ** and **, and it considered as evaluation of endurance.

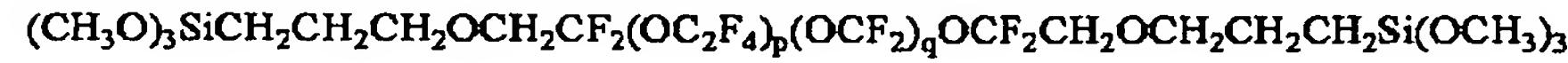
(3) After pressing the index finger against the evaluation stain-proofing barrier front face of antifouling property for 5 seconds and making a fingerprint adhere, the ease of wiping off of the fingerprint when wiping off the fingerprint with the dry cloth was evaluated. By the following valuation bases, five test subjects' average was considered as the evaluation.

x in which marks do not remain although it is hard to wipe off **:fingerprint which can wipe off
 O:fingerprint lightly in the ease of wiping off of a fingerprint: A fingerprint is [0071] in which marks also remain that it is hard to wipe off. The following compounds 2-4 were used instead of the perfluoro polyether denaturation silane of the compound 1 used in the [examples 1-3 of comparison] example, and also the same approach as an example estimated. An evaluation result is shown in Table 1.

[0072]

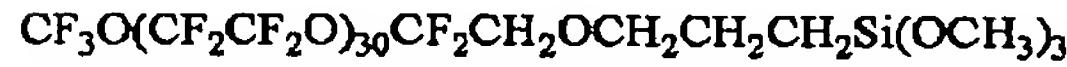
[Formula 14]

化合物 1



$$p/q \approx 0.9 \quad p+q \approx 4.5$$

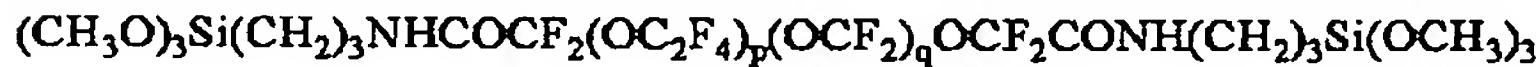
化合物 2



化合物 3



化合物 4



$$p/q \approx 0.6 \quad p+q \approx 6.0$$

[0073]

[Table 1]

		転落角(deg)		接着力(N/19mm)		指紋拭き取り性
		洗净前	洗净後	洗净前	洗净後	
実施例	化合物1	1.8	1.8	0.12	0.14	O
比較例	化合物2	2.5	11.3	0.10	0.37	O
	化合物3	3.4	10.4	0.19	0.37	△
	化合物4	6.2	6.5	0.29	0.34	△

[0074] An example has a surface characteristic beyond the example of a comparison, and is excellent in endurance and fingerprint wiping nature.

[0075]

[Effect of the Invention] Since the perfluoro polyether denaturation silane in this invention does not contain in a molecule the polar group which can serve as an adverse element in respect of a property, it is excellent in water and oil repellency, a mold-release characteristic, chemical resistance, lubricity, endurance, antifouling property, and fingerprint wiping nature, can be used as a finishing agent with which various base material front faces are coated, and can be applied to the acid-resisting filter in which the hardening coat was formed on the front face. Moreover, the acid-resisting filter of this invention cannot become dirty easily, tends to wipe off the dirt, surface slipping nature is good, and cannot get damaged easily, and it has the descriptions, such as making those engine performance into a long period of time, for example, can use them for various kinds of optical elements, such as various kinds of check-by-looking equipments, such as LCD, and a polarizing plate.

[0076]

[Translation done.]

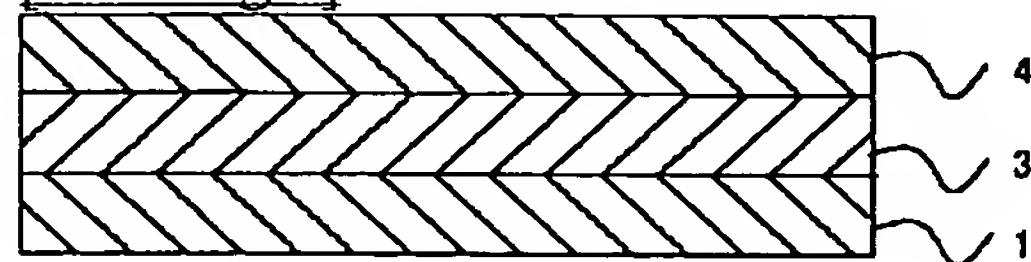
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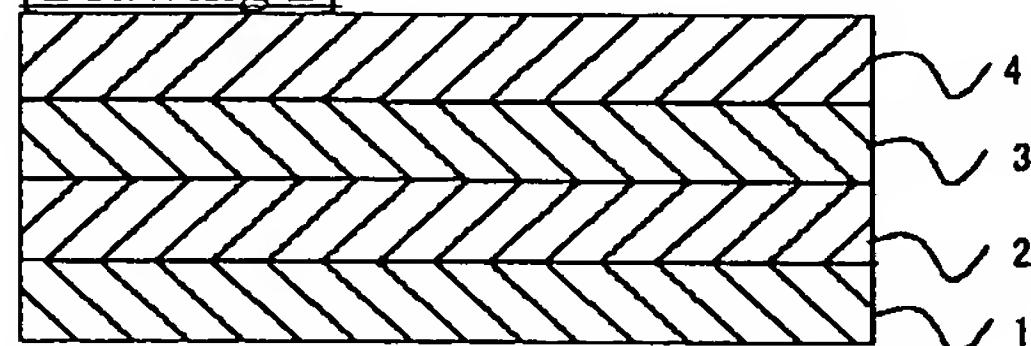
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
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DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

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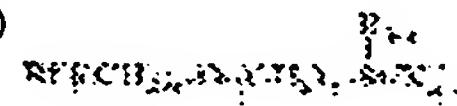
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(54) PERFLUOROPOLYETHER-MODIFIED SILANE, SURFACE TREATING AGENT AND ANTIREFLECTION FILTER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a perfluoropolyether-modified silane which has water/oil repellency, parting properties, chemical resistance, lubricity, durability, antifouling properties and fingerprint wipe-off property due to absence of a polar group, is useful as a surface treating agent for coating the surfaces of various kinds of substrates, is applicable to an antireflection filter that has been formed with a cured coating film on the surface, is hardly stained, has the stain to be readily wiped off, is excellent in slipperiness on the surface, is hardly damaged and keeps these performances for a long period of time.

SOLUTION: The perfluoropolyether-modified silane is represented by formula (1) (Rf is a bifunctional straight-chain perfluoropolyether group; R is a 1-4C alkyl group or phenyl group; X is a hydrolyzable group; (n) is 0-2; (m) is an integer of 1-5; (a) is 2 or 3).



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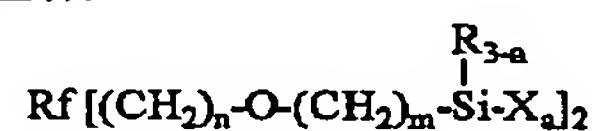
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最終頁に続く

(54)【発明の名称】パーフルオロポリエーテル変性シラン及び表面処理剤、並びに反射防止フィルター

(57)【要約】 (修正有)

【解決手段】 下記一般式 (1)



(式中、Rfは二価の直鎖型パーフルオロポリエーテル基、Rは炭素数1～4のアルキル基又はフェニル基、Xは加水分解性基、nは0～2、mは1～5の整数、aは2又は3である。)で示されるパーフルオロポリエーテル変性シラン。

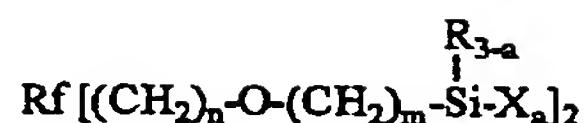
【効果】 本発明におけるパーフルオロポリエーテル変性シランは、極性基を含まないことから、撥水撥油性、離型性、耐薬品性、潤滑性、耐久性、防汚性、指紋拭き

取り性に優れており、各種基材表面にコーティングする表面処理剤として利用することができ、硬化被膜を表面に形成した反射防止フィルターに応用することができる。また、本発明の反射防止フィルターは、汚れにくく、その汚れを拭き取り易く、表面の滑り性が良好で傷付きにくく、それらの性能を長期に持続するなどの特徴を有する。

(1)

【特許請求の範囲】

【請求項1】 下記一般式(1)

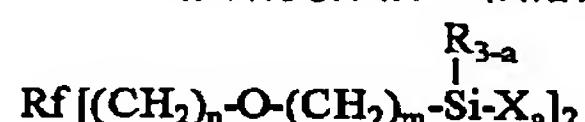


(式中、R_fは二価の直鎖型パーフルオロポリエーテル基、Rは炭素数1～4のアルキル基又はフェニル基、Xは加水分解性基、nは0～2、mは1～5の整数、aは2又は3である。)で示されるパーフルオロポリエーテル変性シラン。

【請求項2】 加水分解性基Xがオルガノオキシ基であることを特徴とする請求項1記載のパーフルオロポリエーテル変性シラン。

【請求項3】 請求項1又は2記載のパーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物を主成分とする表面処理剤。

【請求項4】 表面層として二酸化ケイ素系無機層を有する無機系反射防止層の表面層上に、オレイン酸に対する転落角が5°以下であり、且つ、溶剤洗浄前の転落角



(式中、R_fは二価の直鎖型パーフルオロポリエーテル基、Rは炭素数1～4のアルキル基又はフェニル基、Xは加水分解性基、nは0～2、mは1～5の整数、aは2又は3である。)で示される化合物であることを特徴とする請求項6記載の反射防止フィルター。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、撥水撥油性、離型性、耐薬品性、潤滑性などに優れ、かつ耐久性、防汚性、特に指紋拭き取り性に優れた新規なパーフルオロポリエーテル変性シラン及びこれを主成分とする表面処理剤、並びに防汚性、指紋拭き取り性に優れ、特に耐久性に優れた防汚層を有する反射防止フィルターに関する。

【0002】

【従来の技術】 一般にパーフルオロポリエーテル基含有化合物は、その表面エネルギーが非常に小さいために、撥水撥油性・耐薬品性・潤滑性・離型性・防汚性などを有する。その性質を利用して、工業的には紙・繊維などの撥水撥油防汚剤、磁気記録媒体の滑剤、精密機器の防油剤、離型剤、化粧料、保護膜などに幅広く利用されて

40

【化1】

(1)

に対する溶剤洗浄後の転落角の変化率が10%以下である防汚層を形成したことを特徴とする反射防止フィルター。

【請求項5】 防汚層の粘着テープに対する接着力及び溶剤洗浄後の防汚層の粘着テープに対する接着力がそれぞれ0.2N/19mm以下であることを特徴とする請求項4記載の反射防止フィルター。

【請求項6】 防汚層が、パーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物を用いて形成されることを特徴とする請求項4又は5記載の反射防止フィルター。

【請求項7】 パーフルオロポリエーテル変性シランが、下記一般式(1)

【化2】

(1)

いる。

【0003】 しかし、その性質は同時に他の基材に対する非粘着性、非密着性があることを示しており、基材表面に塗布することはできても、被膜を形成し密着させることは困難であった。

【0004】 一方、ガラスや布などの基材表面と有機化合物とを結合させるものとしては、シランカップリング剤が良く知られている。シランカップリング剤は、1分子中に有機官能基と反応性シリル基(一般にはアルコキシリル基)を有する。アルコキシリル基は、空気中の水分などによって自己縮合反応をおこしてシロキサンとなり被膜を形成する。それと同時に、ガラスや金属などの表面と化学的・物理的に結合することによって、耐久性を有する強固な被膜となる。シランカップリング剤はこの性質を利用して各種基材表面のコーティング剤として幅広く利用されている。

【0005】 これらの特徴を生かしたものとして、特開昭58-167597号公報では、下記式(2)

【化3】

(2)

O)の2～5量体と短いため、上記パーフルオロポリエーテル基の持つ特徴を十分に出すことができなかった。

【0006】 また、特開昭58-122979号公報では、ガラス表面の撥水撥油剤として下記式(3)

【化4】

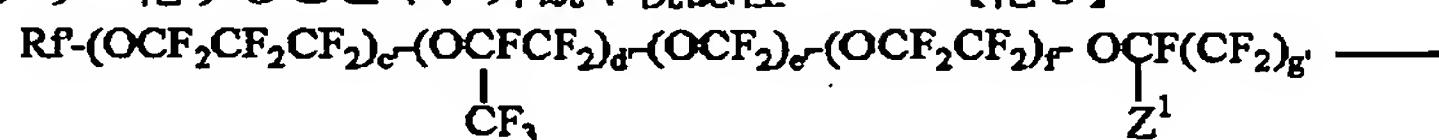
(式中、R¹、R²は炭素数1～4のアルキル基、Q¹はCH₂、CH、CH₂又はCH、CH、NHCH、CH、CH₂、CH₃、hは1～4の整数、iは2又は3である。)で示されるフルオロアミノシラン化合物が開示されている。しかしながら、この化合物は、パーフルオロポリエーテル基の部分が、ヘキサフルオロプロピレンオキサイド(HFP)

50



(式中、 Rf' は炭素数1～20個のポリフルオロアルキル基であってエーテル結合を1個以上含んでもよい。 R' は水素原子又は低級アルキル基、Aはアルキレン基、 X' は $-CON(R')$ —Q—又は $SO, N(R')$ —Q—(但し、 R' は低級アルキル基、Qは2価の有機基を示す)、Zは低級アルキル基、Yはハロゲン、アルコキシ基又は $R'COO-$ (但し、 R' は水素原子又は低級アルキル基を示す)、sは0又は1の整数、tは1～3の整数、uは0又は1～2の整数を示す。)で示される化合物が提示されているが、この場合も含フッ素基の部分の炭素数が1～20個と少なく、十分な効果が得られない。

【0007】特に最近では、建築物の高層化に伴い窓ガラスをメンテナンスフリー化することや、外観や視認性

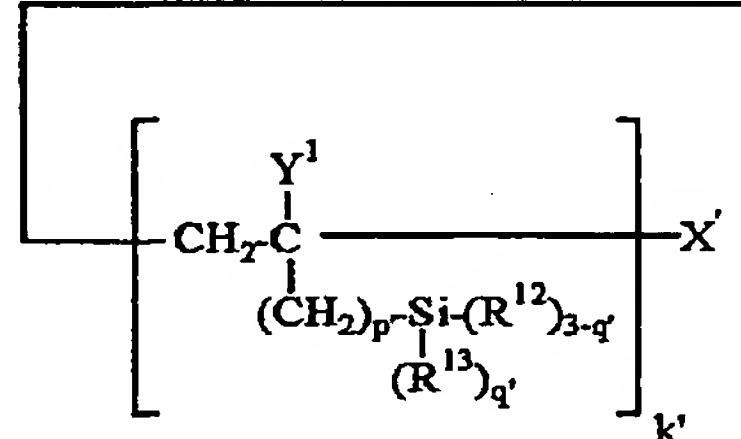
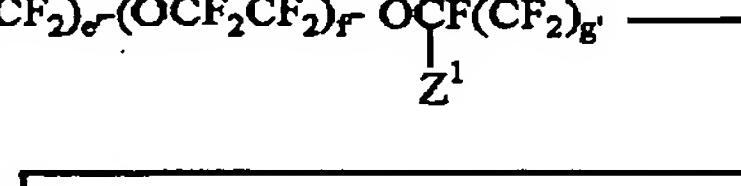


をよくするためにディスプレイの表面に指紋が付きにくくするなど「汚れにくくする」技術や、「汚れを落とし易くする」技術に対する要求は年々高まってきており、これらの要求に応えることのできる材料の開発が望まれていた。

【0008】上記パーフルオロポリエーテル基含有化合物及びシランカップリング剤の特性を活かし、基材表面に強固な被膜を形成し、撥水撥油性、防汚性、耐薬品性、潤滑性、離型性等に優れた表面処理剤として、下記式(4)で表される含フッ素シラン化合物を防汚層に用いたレンズが知られている(特開平9-258003号公報)。

【0009】

【化5】



(4)

(式中、 Rf' は炭素数1～16の直鎖状又は分岐状パーフルオロアルキル基、 X' はヨウ素又は水素、 Y' は水素又は低級アルキル基、 Z' はフッ素又はトリフルオロメチル基、 R^{12} は加水分解可能な基、 R^{13} は水素又は不活性な一価の有機基、c'、d'及びf'は0～20の整数、g'は0又は1、p'及びq'は0～2の整数、k'は1～10の整数を示す。)

【0010】しかし、上記一般式(4)で表される含フッ素シラン化合物は、1分子中の加水分解性基の含有割合は比較的多いものの、片末端にしか存在しないことから、特に基材への密着性が不十分で耐久性の点で問題があり、レンズの表面処理剤として利用した場合には、所望の性能を長期間にわたって持続させ得るものではなく適切なものとはいえないかった。

【0011】また、視認装置等の表面に設けられることが一般的な反射防止膜にあっては、手垢や指紋、汗や唾液、整髪料等の汚染物が付着し易く、その付着で表面反射率が変化したり、付着物が白く浮き出て見て表示内容が不鮮明になるなど、単なる透明板等の場合に比べて汚染が目立ち易いという難点があるため、かかる汚染物の付着防止性や付着汚染の除去性に優れる反射防止膜の提供が久しい課題となっている。

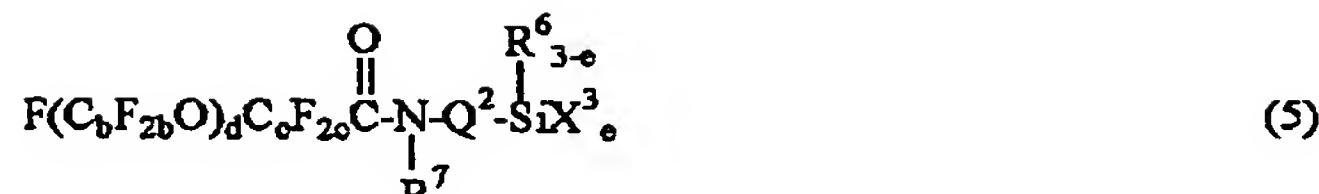
【0012】従来、耐汚染性の向上等を目的とした反射防止膜としては、PVD法により形成した二酸化ケイ素

を主成分とする表面層を有する単層又は多層の無機物層からなる反射防止層の表面に、有機ポリシロキサン系重合物又はパーフルオロアルキル基含有重合物からなる硬化層を有するものが知られていた(特公平6-5324号公報)。

【0013】しかしながら、手垢や指紋等の人体的汚染が付着した場合に、ティッシュペーパーなどで拭き取ることが困難で、汚染が薄膜に押し抜けられ、強く擦ると反射防止膜が傷付くため、満足できる除去を達成できないという問題点があった。

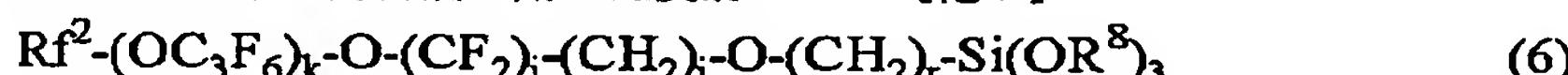
【0014】一般に、パーフルオロポリエーテル基含有化合物は、前述の特徴を有するもので、これらの特徴を生かしたものとして、特開平11-29585号公報では、下記式(5)で示されるパーフルオロポリエーテル変性アミノシランを防汚層に用いた反射防止膜が開示されている。しかし、この反射防止膜は、撥水撥油性、防汚性、耐薬品性、潤滑性、離型性等に優れているものの、防汚層に用いたパーフルオロポリエーテル変性アミノシランの分子中に水との親和性の高いアミド基等の極性基を含有しており、また、1分子中の加水分解性基の割合(重量%)が少ないため、硬化までに時間を要することや、基材への密着性の点などの問題点を有し、表面処理剤として利用する上で更に十分な性能を与えることが望まれた。

【化6】



(式中、 X^3 は加水分解性基、 R^6 は低級アルキル基、 R^7 は水素原子又は低級アルキル基、 Q^2 は CH_2 、 CH 、 CH_3 又は CH_2CH 、 $NHCH_2$ 、 CH_2CH_2 、 d は6～50の整数、 e は2又は3、 b 及び c はそれぞれ1～3の整数。)

【0015】また、特開平2001-188102号公報では、下記式(6)で示されるパーフルオロポリエーテル基含有シランカップリング剤を防汚層に用いた反射



(但し、 Rf^2 は炭素数1～16の直鎖状又は分岐状パーフルオロアルキル基、 R は炭素数1～10のアルキル基、 k は1～50の整数、 r は0～6の整数、 j は0～3の整数、 i は0～3の整数であるが、 $0 < j + i \leq 6$ である。)

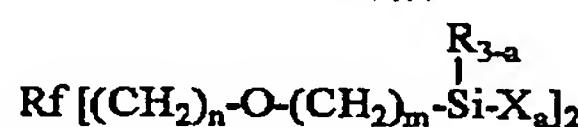
【0016】よって、汚染が付着しにくく、かつ汚染が付着した場合にもその汚染が目立ちにくくと共に、手垢や指紋などの人体的汚染も含めて付着した汚染をティッシュペーパー等で容易に拭き取り除去でき、その拭き取り操作で傷付きにくくて、水滴等の付着は容易に振り落とすことができ、しかもかかる耐汚染性や易拭き取り除去性、耐擦傷性や撥水性等の性能を長期に持続する反射防止フィルターの開発が望まれていた。

【0017】

【特許文献1】特開昭58-167597号公報

【特許文献2】特開昭58-122979号公報

【特許文献3】特開平9-258003号公報



(式中、 Rf は二価の直鎖型パーフルオロポリエーテル基、 R は炭素数1～4のアルキル基又はフェニル基、 X は加水分解性基、 n は0～2、 m は1～5の整数、 a は2又は3である。)で表される新規なパーフルオロポリエーテル変性シランが、撥水撥油性、離型性、耐薬品性、潤滑性、耐久性、防汚性、特に指紋拭き取り性に優れており、表面処理剤として利用でき、反射防止フィルターの表面に硬化膜を形成することに適していることを知見し、本発明をなすに至った。

【0020】また、二酸化ケイ素系無機層を有する無機系反射防止層の表面層上に防汚層を形成すること、この場合、上記式(1)のシランを用いるなどして、防汚層を、オレイン酸に対する転落角が5°以下であり、且つ、溶剤洗浄前の転落角に対する溶剤洗浄後の転落角の変化率が10%以下のものとすることで、表面エネルギーが小さく、汚染物質の付着力が小さい上に、その効果

防止フィルムが開示されており、この防汚層に用いられるパーフルオロポリエーテル基含有シランカップリング剤は、極性基は含有していないものの、1分子中の加水分解性基の割合が十分とは言えず、硬化までに時間を要することや、基材への密着性が劣るなど、表面処理剤として利用する上で十分な性能を有しているとは言えなかった。

【化7】

10 防止フィルムが開示されており、この防汚層に用いられるパーフルオロポリエーテル基含有シランカップリング剤は、極性基は含有していないものの、1分子中の加水分解性基の割合が十分とは言えず、硬化までに時間を要することや、基材への密着性が劣るなど、表面処理剤として利用する上で十分な性能を有しているとは言えなかった。

【化7】

【特許文献4】特公平6-5324号公報

【特許文献5】特開平11-29585号公報

【特許文献6】特開平2001-188102号公報

【0018】

20 【発明が解決しようとする課題】従って、本発明は、上記要望に応えるべく、撥水撥油性、離型性、耐薬品性、潤滑性などに優れ、かつ耐久性、防汚性、特に指紋拭き取り性に優れた新規なパーフルオロポリエーテル変性シラン及びこれを主成分とする表面処理剤、並びに防汚性、指紋拭き取り性に優れ、特に耐久性に優れた防汚層を表面に有する反射防止フィルターを提供することを目的とする。

【0019】

【課題を解決するための手段及び発明の実施の形態】本発明者は、上記要望に応えるために鋭意検討を行った結果、下記一般式(1)

【化8】

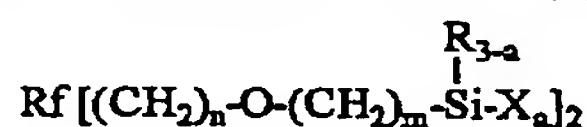
(1)

が持続し、また、指紋、皮脂、汗、化粧品などの汚染物質の付着を防止し、また、付着しても容易に拭き取れるようになり、擦過による防汚層の機能低下が少なく、反射防止層表面に傷が付き難く、傷をきっかけとした反射防止層の剥離を防ぐことができる反射防止フィルターが得られることを知見し、本発明をなすに至った。

【0021】従って、本発明は、上記一般式(1)のパーフルオロポリエーテル変性シランを提供する。また、このパーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物を主成分とする表面処理剤、並びに表面層として二酸化ケイ素系無機層を有する無機系反射防止層の表面層上に、オレイン酸に対する転落角が5°以下であり、且つ、溶剤洗浄前の転落角に対する溶剤洗浄後の転落角の変化率が10%以下である防汚層、特に上記式(1)のシラン及び/又はその部分加水分解縮合物を用いた防汚層を形成したことを特徴とする反射防

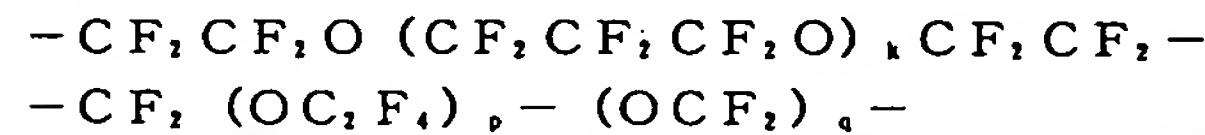
止フィルターを提供する。

【0022】以下、本発明につき更に詳しく述べる。
本発明のパーフルオロポリエーテル変性シランは、下記



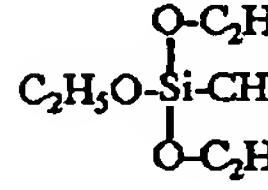
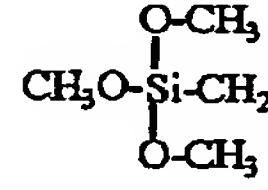
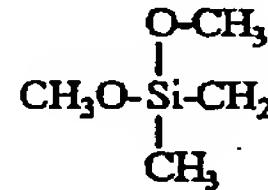
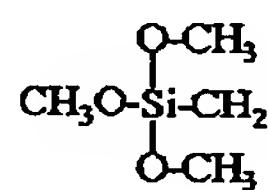
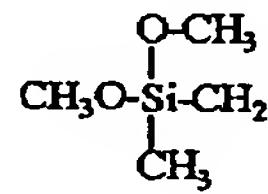
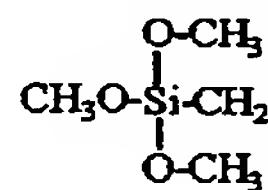
(式中、Rfは二価の直鎖型パーフルオロポリエーテル基、Rは炭素数1～4のアルキル基又はフェニル基、Xは加水分解性基、nは0～2、mは1～5の整数、aは2又は3である。)

【0024】ここで、Rfは、二価の直鎖型パーフルオロポリエーテル基であり、各種鎖長のパーフルオロポリエーテル基が含まれるが、好ましくは炭素数1～4程度のパーフルオロポリエーテル基を繰返し単位とする二価の直鎖型パーフルオロポリエーテルである。この二価の直鎖型パーフルオロポリエーテルとしては、例えば、以下に示すようなものが挙げられる。



上記化学構造式中のk、p及びqはそれぞれ1以上の整数を示す。具体的には1～50、より好ましくは10～40の範囲が好ましい。なお、パーフルオロポリエーテルの分子構造は、これら例示したものに限定されるものではない。

【0025】Xは加水分解性基を表す。その具体例としては、メトキシ基、エトキシ基、プロポキシ基、ブトキシ基などのアルコキシ基、メトキシメトキシ基、メトキシエトキシ基などのアルコキシアルコキシ基、アセトキ



(上記式中、Lは1～50、pは1～50、qは1～50、p+qの和は10～100の整数であり、式中の繰り返し単位の配列はランダムである。) これらは1種單

一般式(1)で示されるものである。

【0023】
【化9】

(1)

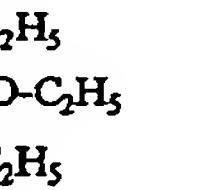
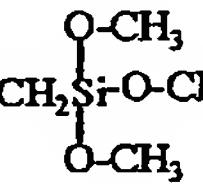
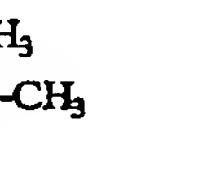
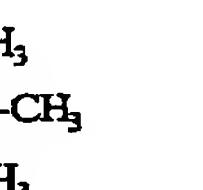
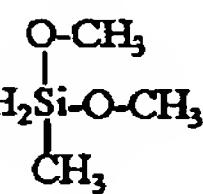
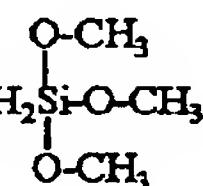
シ基などのアシロキシ基、イソプロペノキシ基などのアルケニルオキシ基、クロル基、プロモ基、ヨード基などのハロゲン基などが挙げられる。中でもアルコキシ基、アルケニルオキシ基等のオルガノオキシ基、クロル基が好ましく、特にメトキシ基、エトキシ基、イソプロペノキシ基、クロル基が好ましい。

【0026】Rは、炭素数1～4の低級アルキル基又はフェニル基で、具体的にはメチル基、エチル基、フェニル基などであり、中でもメチル基が好適である。nは0～2の整数であり、1が好ましい。また、mは1～5の整数であり、3が好ましい。aは2又は3であり、反応性、基材に対する密着性の観点から、3が好ましい。

【0027】本発明のパーフルオロポリエーテル変性シラン化合物の分子量は、特に制限されないが、安定性、取扱い易さ等の点から、数平均分子量で500～2万、好ましくは1000～1万のものが適当である。

【0028】上記パーフルオロポリエーテル変性シランの具体例としては、例えば、下記構造式で示されるものが挙げられる。但し、下記例示に限定されるものではない。

【0029】
【化10】



独でも2種以上を組み合わせても使用することができる。

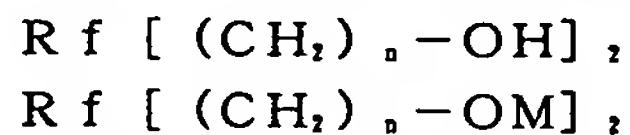
【0030】本発明のパーフルオロポリエーテル変性シ

ランの製造方法としては、例えば、両末端に α -不飽和結合を含有するパーフルオロポリエーテルに加水分解性基を有するヒドロシランを、白金系触媒を用いたヒドロ



(式中、Rf、R、X、n、m及びaは前記と同じである。)

【0032】ここで、上記両末端に α -不飽和結合を含有するパーフルオロポリエーテルの合成方法としては、下記式(7)で表される両末端アルコール変性パーフルオロポリエーテルを、K、Na、Li等のアルカリ金



(式中、nは前記と同じ、Mはアルカリ金属である。)

【0033】本発明のパーフルオロポリエーテル変性シランは、分子中に特性面ではマイナス要因となり得る極性基を全く含まないことから、撥水撥油性、防汚性、耐薬品性、潤滑性、離型性等に優れており、各種基材表面にコーティングすることにより表面処理剤として利用することができる。また、分子の両末端に加水分解性のシリル基等の加水分解性基を少なくとも2個ずつ有しており、両末端が基材に強固に密着しているため、その効果を長期間持続させることができる。

【0034】この機能を利用した応用例として、次のようなものが挙げられる。

撥水撥油剤…紙・布・金属・ガラス・プラスチック・セラミックなど、

離型剤…粘着テープ用・樹脂成形用金型・ロール用など、

防汚加工剤…紙・布・金属・ガラス・プラスチック・セラミックなど、

その他…塗料添加剤、樹脂改質剤、無機質充填材の流動性・分散性を改質、テープ・フィルムなどの潤滑性の向上など。

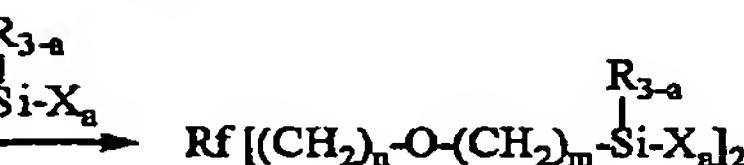
【0035】本発明のパーフルオロポリエーテル変性シランは、表面処理剤として好適に用いられ、反射防止フィルターの表面に硬化被膜を形成することができる。本発明の表面処理剤は、本発明の式(1)に示すパーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物を主成分とする。

【0036】この表面処理剤には、必要に応じてオルガノオキシシラン加水分解縮合触媒を添加してもよい。オルガノオキシシラン加水分解縮合触媒としては、ジブチル錫ジメトキシド、ジラウリン酸ジブチル錫などの有機錫化合物、テトラ n -ブチルチタネートなどの有機チタン化合物、酢酸、メタンスルホン酸などの有機酸、塩酸、硫酸などの無機酸が挙げられる。特に酢酸、テトラ n -ブチルチタネート、ジラウリン酸ジブチル錫などが好ましい。添加量は通常の触媒量であり、パーフルオロ

シリル化の常法より付加させる方法がある。

【0031】

【化11】



属、KOH、NaOH、LiOH等のアルカリ金属水酸化物と反応させて、式(8)で表される両末端アルコラート変性パーフルオロポリエーテルを生成させ、次にこの両末端アルコラート変性パーフルオロポリエーテルを α -不飽和結合含有ハロゲン化物と反応させることにより得られる。

(7)

(8)

ポリエーテル変性シラン及び/又はその部分加水分解縮合物100重量部に対して0.01~5重量部が好ましく、特に0.1~1重量部が好ましい。

【0037】また、本発明の処理剤は、パーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物をそのまま使用してもよいが、適当な溶剤で希釈してもよい。溶剤は2種以上の混合溶剤でもよく、パーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物を、均一に溶解させるものが望ましい。

【0038】溶剤としては、パーフルオロヘプタン、パーフルオロオクタンなどのフッ素変性脂肪族炭化水素系溶剤、m-キシレンヘキサフロライド、ベンゾトリフロライドなどのフッ素変性芳香族炭化水素系溶剤、メチルパーフルオロブチルエーテル、パーフルオロ(2-ブチルテトラヒドロフラン)などのフッ素変性エーテル系溶剤、パーフルオロトリブチルアミン、パーフルオロトリペンチルアミンなどのフッ素変性アルキルアミン系溶剤、石油ベンジン、ミネラルスピリット、トルエン、キシレンなどの炭化水素系溶剤、アセトン、メチルエチルケトン、メチルイソブチルケトンなどのケトン系溶剤が挙げられる。溶解性、濡れ性などの点で、フッ素変性された溶剤が好ましく、特に、m-キシレンヘキサフロライド、パーフルオロ(2-ブチルテトラヒドロフラン)、パーフルオロトリブチルアミンが好ましい。

【0039】被膜を形成する方法としては、刷毛塗り、ディッピング、スプレー、蒸着処理など公知の方法で処理できる。処理温度は、処理方法によって最適な温度は異なるが、例えば刷毛塗りやディッピングの場合は、室温から120℃の範囲が好ましい。処理湿度は、加湿下で行なうことが反応を促進する上で好ましいが、使用するシラン化合物や他の添加剤によってその都度最適化することが好ましい。

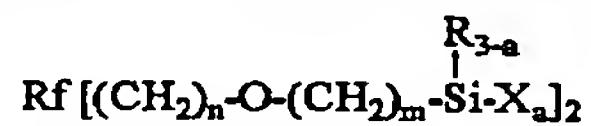
【0040】被膜を形成する基材としては、紙、布、金属及びその酸化物、ガラス、プラスチック、陶磁器、セラミックなど各種材質のものを用いることができる。

【0041】ここで、硬化被膜を表面に形成する物品と

しては、めがねレンズ、反射防止フィルターなど光学部材（指紋、皮脂付着防止コーティング）、浴槽、洗面台のようなサニタリー製品（撥水、防汚コーティング）、自動車、電車、航空機などの窓ガラス、ヘッドランプカバーなど（防汚コーティング）、外壁用建材（撥水、防汚コーティング）、台所用建材（油汚れ防止用コーティング）、電話ボックス（撥水、防汚及び貼り紙防止コーティング）、美術品など（撥水・撥油性、及び指紋付着防止付与のコーティング）、コンパクトディスク、DVD（指紋付着防止コーティング）などが好ましい。特に、レンズ、フィルターなどの光学部材に被膜を形成し、反射防止性、防汚性などを付与するには本発明の表面処理剤は好適である。

【0042】本発明は、更に反射防止フィルター、特に上記式（1）のパーフルオロポリエーテル変性シラン及び/又はその部分加水分解縮合物の硬化被膜を表面に有する反射防止フィルターを提供する。この場合、本発明の反射防止フィルターは、表面層として二酸化ケイ素系無機層を有する反射防止層の表面に防汚層を形成したもので、前記防汚層として、オレイン酸に対する転落角が5°以下であり、且つ、溶剤洗浄前の転落角に対する溶剤洗浄後の転落角の変化率が10%以下であるものを使用することを特徴とする。

【0043】ここで、防汚層は、オレイン酸に対する転落角が5°以下、好ましくは3°以下であり、且つ、溶剤洗浄前の転落角に対する溶剤洗浄後の転落角の変化率が10%以下、好ましくは5%以下である。オレイン酸に対する転落角が5°より大きいと、汚染防止性に乏し



（式中、R_fは二価の直鎖型パーフルオロポリエーテル基、Rは炭素数1～4のアルキル基又はフェニル基、Xは加水分解性基、nは0～2、mは1～5の整数、aは2又は3である。）

【0047】防汚層を形成する方法としては、刷毛塗り、ディッピング、スプレー、蒸着処理など公知の方法の処理が挙げられる。処理温度は、処理方法によって最適な温度は異なり、例えば刷毛塗りやディッピングの場合、室温から120℃の範囲が好ましい。処理湿度は、加湿下で行なうことが反応を促進する上で好ましいが、使用するシラン化合物や他の添加剤によって処理条件は異なるため、その都度最適化することが好ましい。

【0048】この様な塗布作業において、パーフルオロポリエーテル変性シランをそのまま使用してもよいが、適当な溶剤で希釈して用いてもよい。溶剤は2種以上の混合溶媒でもよく、パーフルオロポリエーテル変性シランを均一に溶解させるものが好ましい。

【0049】溶剤としては、上記した溶剤と同様のものを使用することができる。また、更に必要に応じて、上記したものと同様のオルガノオキシシラン加水分解縮合

く、特に指紋等が付着し易く、また汚染の拭き取り性に乏しくなり、また拭き取りの際の表面での滑り性に乏しい場合がある。

【0044】溶剤洗浄前の転落角Aに対する溶剤洗浄後の転落角Bの変化率 [(B-A)/A] × 100が10%を超えると、汚染防止性及び指紋拭き取り性に関して、耐久性に乏しい場合がある。なお、オレイン酸に対する転落角は、通常用いられる接触角計で測定する。また、溶剤洗浄は、該当溶剤中に5分間浸漬後、軽く掛流す方法で行ない、溶剤は通常の洗浄で用いられるものでよく、例えば、HCFC-225、ノナフルオロブチルメチルエーテル等が挙げられる。

【0045】また、防汚層の粘着テープに対する接着力及び溶剤洗浄後の防汚層の粘着テープに対する接着力がそれぞれそれぞれ0.2N/19mm以下であることが好ましい。防汚層の粘着テープに対する接着力が0.2N/19mmより大きいと、指紋拭き取り性に乏しい場合がある。防汚層の粘着テープに対する接着力は、防汚層表面にポリエステル粘着テープで、引張試験機を用いて180°の角度で剥離速度300mm/minで測定する。

【0046】この場合、防汚層は、パーフルオロポリエーテル変性シランを用いて形成されることが好ましく、特に前述と同様の下記一般式（1）で示されるパーフルオロポリエーテル変性シラン又はその部分加水分解物の硬化皮膜が好ましい。

【化12】

(1)

触媒を添加してもよい。

【0050】なお、防汚層の膜厚は、適宜選定されるが、通常0.1nm～5μm、特に1～100nmが好ましい。

【0051】本発明の反射防止フィルターは、表面層として二酸化ケイ素系無機層を有する無機系反射防止層の表面層上に上記のように防汚層を形成する反射防止フィルターであるが、この場合、無機系反射防止層は、支持基材上に直接又はハードコート層等の中間層を介して設けることが好ましい。図1、2は、これを示すもので、図中1は支持基材、2は中間層、3は無機系反射防止層、4は防汚層である。

【0052】ここで、無機系反射防止層は、実質的な反射防止機能を担う部分であり、本発明においては、単層構造又は複層構造の適宜な構造とすることができますが、反射防止膜の表面層は二酸化ケイ素系無機層である。

【0053】従って、無機系反射防止層としては、例えば特開昭58-46301号公報、特開昭59-49501号公報や特開昭58-50401号公報、特開平1-294709号公報や特開平6-5324号公報など

に基く従来技術の如く、従来に準じた構造の反射防止層として形成することができる。

【0054】反射防止層は、反射防止効果等の点より、複層構造とすることが好ましく、特に、表面層の二酸化ケイ素系無機層よりも高い屈折率の層を1層又は2層以上内在させた複層構造とすることが好ましい。その場合、各層の厚さや屈折率の設定等については、公知技術に準じることができる。

【0055】無機系反射防止層の形成には、無機酸化物、無機ハロゲン化物、それらの複合物等よりなる無機物を用いることができる。その具体例としては、 SiO_2 、 ZrO_2 、 Al_2O_3 、 Y_2O_3 、 TiO_2 等の無機酸化物、 MgF_2 、 BaF_2 、 CaF_2 、 LaF_3 、 LiF 、 NaF 、 SrF_2 等の無機ハロゲン化物などが代表例として挙げられる。

【0056】反射防止層を形成する無機物は、下記の形成方法などに応じてその1種又は2種以上が固体物、あるいはバインダー用ポリマー等と混合した分散液などの適宜の状態で用いられるが、その場合、無機物を30重量%以上含有する組成で用いることが、硬度や耐汚染性などの点より好ましい。なお、バインダー用ポリマーとしては、適宜のポリマーを用いることができ、特に限定はないが、硬度等の点より、ポリオルガノシロキサンを形成しうる各種の有機ケイ素化合物やその加水分解物などが好ましい。

【0057】無機系反射防止層の形成は、例えば真空蒸着法、スパッタリング法、イオンプレーティング法等で代表される各種のPVD (Physical Vapour Deposition) 法、あるいはスピンドル法、浸漬コート法、カーテンフローコート法、ロールコート法、スプレーコート法、流し塗り法等で代表される流体塗布法などの適宜な薄膜形成法にて行うことができる。

【0058】PVD法には、上記に例示した SiO_2 等の無機酸化物や MgF_2 等の無機ハロゲン化物などが好ましく用いられ、特に表面層となる二酸化ケイ素系無機層は、表面硬度の高さや防汚層の密着性などの点より、PVD法により二酸化ケイ素を主成分として含有する層

$R^f, R^{10}, Si(O R^{11})_{1-10}$

(式中、 R^f 、 R^{10} はアルキル基、アルケニル基、アリール基、又はハロゲン基、エポキシ基、グリシドキシ基、アミノ基、メルカブト基、メタクリルオキシ基、シアノ基等を有する炭化水素基などであり、 R^{11} は炭素数1~8のアルキル基、アルコキシアルキル基、アシル基、又はアリール基などである。f、gは0又は1であり、f+gは、0、1又は2である。)

【0064】ハードコート層は、例えばソルゲル法などにより平均粒径が0.5~5μmのシリカや金属酸化物などの微粒子を含有させる方法、あるいはバフ、コロナ放電、イオンエッティングの如き適宜な方法で、中心線

に形成したものが好ましい。

【0059】また、無機系反射防止層には、帶電によるゴミ等の付着を防止するために静電気の除去効果や電磁波のシールド効果も発揮する導電層を含ませてもよい。かかる導電層は、例えば金、銀、アルミニウム等の金属薄膜、酸化スズ、酸化インジウム、それらの混合物(ITO)等の無機酸化物薄膜などからなる透明導電膜として形成される。可視領域では、光の吸収が極めて少ない無機酸化物系の透明導電膜が特に好ましい。

【0060】一方、支持基材としては適宜なものを用いてよく、特に限定はないが、液状コーティング法等で反射防止膜を形成する場合などには、ガラスやプラスチックからなる支持基材が好ましく用いられる。なお、図では、支持基材1の片面に無機系反射防止層3を設けてなる反射防止フィルターを例示したが、支持基材1の片面又は両面に無機系反射防止層3を設けてよい。

【0061】支持基材がガラス基材の場合には、反射防止層に MgF_2 や CaF_2 等の低屈折率を示すものを含ませることが、高い反射効果を得る点などより好ましい。

【0062】支持基材がプラスチック基材の場合には、反射防止層に SiO_2 のような屈折率が比較的低くて硬度の高いものを含ませることが、耐久性などの点より好ましい。プラスチックの例としては、例えば、アクリル系樹脂、ジエチレングリコールビスアリルカーボネート樹脂、ポリカーボネート系樹脂、ポリエチレンテレフタートや不飽和ポリエステル等のポリエステル系樹脂、トリアセチルセルロース等のアセテート系樹脂、スチレン系樹脂、ポリ塩化ビニル系樹脂などが挙げられる。

【0063】ハードコート層も従来に準じて形成することができる。例えば、有機ケイ素化合物、特に下記一般式(9)で示される有機ケイ素化合物やその部分加水分解縮合物の硬化物からなるハードコート層が好ましい。

(9)

平均粗さが0.01~0.5μmの凹凸表面とする方式などにより、防眩機能を有するものとして付設することができる。

【0065】更に、支持基材は、中間層として、ハードコート層に代えて、あるいはハードコート層と共に、例えば反射防止膜の密着性、硬度や耐薬品性、耐久性や染色性等の向上などを目的に、適宜なコート層を有したり、表面処理されたものなどであってよい。

【0066】なお、硬度の向上には、特公昭50-28446号公報、特公昭50-39449号公報、特公昭51-24368号公

報、特公昭57-2735号公報や特開昭52-112698号公報などに記載された高硬度化用の適宜な材料を用いる。また、チタン、アルミニウム、スズ等の金属又はケイ素の酸化物をコーティングする方法や、(メタ)アクリル酸のペンタエリトリトール等による架橋体などのアクリル系架橋体の付設なども硬度の向上に有効である。

【0067】

【実施例】以下、合成例、実施例及び比較例を示し、本発明を具体的に説明するが、本発明は下記の実施例に制限されるものではない。なお、下記の例において部は重量部を示す。



$$p/q \approx 0.9 \quad p+q \approx 4.5$$

【0069】【実施例1】PETフィルム(厚さ: 100 μm)基材上に、シリカゾル135重量部、γ-アグリシドキシプロピルトリエトキシシラン129重量部の加水分解物、γ-クロロプロピルトリメトキシシラン70重量部の加水分解物を主としてなるエタノール溶液に塗布、硬化して、厚さ3 μmのハードコート層を形成した。その上にスパッタリング方式で、SiO₂層、TiO₂層、SiO₂層、TiO₂層、SiO₂層の5層をそれぞれ1/4光学膜厚で順次積層して反射防止層を付設した。次に合成例で得られた上記式(11)で表される化合物1のパーフルオロエーテル変性シラン0.2 gをパーフルオロ(2-ブチルテトラヒドロフラン)99.8 gに溶解させ、コーティング溶液を調製した。この処理液を前記の反射防止層にスピンドルコート法で塗工し、25 °C、湿度70%の雰囲気下で24時間放置して硬化させ防汚層を形成させた。この試料片を用いて、下記(1)～(3)の評価を行なった。結果を表1に示す。

【0070】(1) 表面特性の評価

① 転落角

接触角計(協和界面科学社製CA-A型)を用いて、直径2 mmの大きさからなるオレイン酸液滴の防汚層に対する転落角を測定した。表面上の異なる5ヶ所にて測定を行ない、その平均値で示した。

② 接着力

【0068】【合成例】下記式(10)で表される両末端にα-不飽和結合を有するパーフルオロポリエーテル160 g、メタキシレンヘキサフロライド80 gと塩化白金酸をCH₂=CH-Si(CH₃)₂OSi(CH₃)₂-CH=CH₂で変性した触媒0.1 gに70 °C乾燥エア-雰囲気下でトリメトキシシラン15 gを滴下し、8時間攪拌反応させた後、溶媒を留去したところ、下記式(11)で示される無色透明の液体165 g(粘度: 4.5.5 cSt、比重: 1.730、屈折率: 1.305)が得られた。

【化13】

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化合物1



$$p/q \approx 0.9 \quad p+q \approx 4.5$$

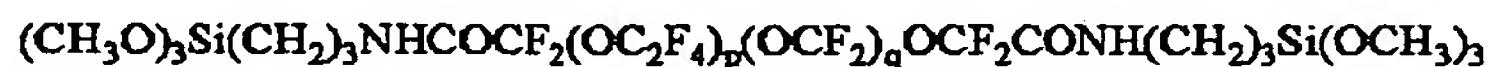
化合物2



化合物3



化合物4



$$p/q \approx 0.6 \quad p+q \approx 6.0$$

【0073】

【表1】

		転落角(deg)		接着力(N/19mm)		指紋拭き取り性
		洗浄前	洗浄後	洗浄前	洗浄後	
実施例	化合物1	1.8	1.8	0.12	0.14	○
比較例	化合物2	2.5	11.3	0.10	0.37	○
	化合物3	3.4	10.4	0.19	0.37	△
	化合物4	6.2	6.5	0.29	0.34	△

【0074】実施例は、比較例以上の表面特性を有し、かつ、耐久性、指紋拭き取り性に優れている。

【0075】

【発明の効果】本発明におけるパーフルオロポリエーテル変性シランは、分子中に特性面ではマイナス要因となり得る極性基を含まないことから、撥水撥油性、離型性、耐薬品性、潤滑性、耐久性、防汚性、指紋拭き取り性に優れており、各種基材表面にコーティングする表面処理剤として利用することができ、硬化被膜を表面に形成した反射防止フィルターに応用することができる。また、本発明の反射防止フィルターは、汚れにくく、その汚れを拭き取り易く、表面の滑り性が良好で傷付きにくく、それらの性能を長期にするなどの特徴を有して、例

えばLCD等の各種の視認装置類や偏光板等の各種の光学素子類に用いることができる。

【0076】

【図面の簡単な説明】

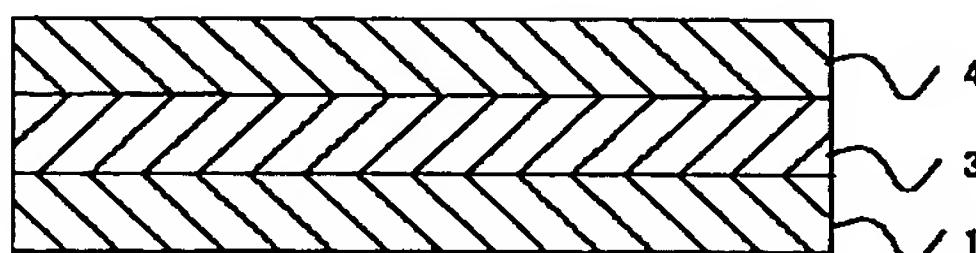
【図1】本発明に係る反射防止フィルターの一例を示す断面図である。

【図2】本発明に係る反射防止フィルターの他の例を示す断面図である。

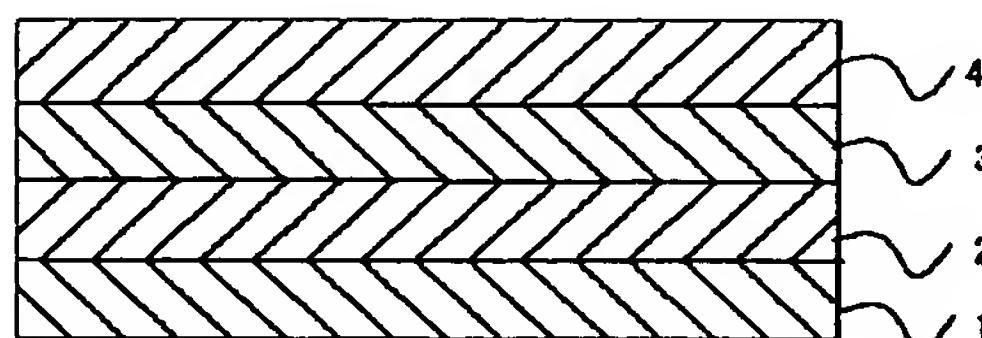
【符号の説明】

- 1 支持基材
- 2 中間層
- 3 無機系反射防止層
- 4 防汚層

【図1】



【図2】



フロントページの続き

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